ESTERIFICATION OF FREE FATTY ACIDS IN SIMULATED WASTE OIL USING NOVEL SOLID ACIDIC IONIC LIQUID AS CATALYST

SHABIRAH BINTI EZAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JULY 2014

ABSTRACT

Issues on petroleum-based fuel shortage can be overcome by producing biodiesel fuel-type or also known as fatty acid methyl ester (FAME). The uses of biodiesel can improve the environmental health and also decrease the worries on the sustainability concerns on world sources of energy (i. e. natural gases). In this study waste cooking oil (WCO); a non-edible type of feedstock was used due to its availability and low cost. Nevertheless, WCO basically has high free fatty acids (FFAs) content which is in the range of 6-15%. Therefore, the study on the esterification of FFAs in a feedstock (WCO) using novel solid acidic ionic liquid as catalyst is carried out to lower the free fatty acid in the WCO. In this case, the use of heterogenous type of acid catalyst is more preferable in the esterification process due to its efficiency. The Bronsted acid ionic liquids (ILs) triethylammonium hydrogen sulphate (Et_3NHSO_4) is chosen to immobilize with solid support, divinylbenzene (DVB) polymer so that it will make separation process smoother and can increase its reusability as a catalyst. The novel solid acidic ionic liquid polymer has been synthesized based on Nuclear Magnetic Resonance (^{1}H-NMR), Elemental Analysis CHNSO and Scanning Electron Microscopy (SEM). The NMR spectroscopic data for the IL sample was: ^{1}H-NMR (500 MHz, DMSO) (ppm): δ 1.08-1.11 (triplet, 0.28H), 1.20-1.23 (triplet, 9.04H), 2.06 (singlet, 0.11H), 2.10 (singlet, 0.03H), 3.09-3.14 (sextet, 6.15H), 3.38-3.4 (doublet, 0.1H), 8.95 (singlet, 1H), 11.00 (singlet, 3.19H). The esterification of the FFA of the WCO was carried out using Et_3NHSO_4 as the catalyst in the first stage at the optimum reaction condition of 60°C reaction temperature, 5 wt % catalysts loading and 6:1 methanol to WCO molar ratio for three hours of reaction time. The novel solid acidic ionic liquid, Et_3NHSO_4 supported with DVB display good performance by showing 75.94 % FFA conversion. It was expected that the recycled catalyst will display the same properties with the fresh catalyst due to its properties that can ease the separation process from the reaction mixture. However, the FTIR result shows the difference of IR spectrum data obtained for the fresh catalyst and spent catalyst which indicates that the catalyst was fully separate from the mixture.

ABSTRAK

Isu-isu kekurangan bahan api berasaskan petroleum boleh diatasi dengan menghasilkan jenis bahan api biodiesel atau juga dikenali sebagai asid lemak metil ester (FAME). Kegunaan biodiesel dapat meningkatkan tahap kesihatan alam sekitar dan juga mengurangkan kebimbangan terhadap masalah pengekalan sumber-sumber. Dalam kajian ini, sisa minyak masak (WCO); bahan mentah jenis yang tidak boleh dimakan telah digunakan kerana ketersediaan dan juga kos rendah. Walau bagaimanapun, WCO pada dasarnya mempunyai asid lemak bebas (FFAs) kandungan tinggi dalam lingkungan 6-15%. Oleh itu, kajian mengenai pengesteran FFAs dalam bahan mentah (WCO) menggunakan novel pepejal cecair berasid ionik sebagai pemangkin dijalankan untuk mengurangkan asid lemak bebas dalam WCO. Dalam kes ini, penggunaan pemangkin jenis asid heterogen adalah lebih lebih baik dalam proses pengesteran kerana ia lebih cekap. Asid Bronsted cecair ionik (ILS) triethylammonium hidrogen sulfat (Et_3NHSO_4) dipilih untuk dilumpuhkan dengan sokongan solid, divinylbenzene (DVB) polimer supaya ia akan menjadikan proses pemisahan lancar dan boleh meningkatkan sistem boleh gunapakai sebagai pemangkin. Novel pepejal berasid polimer cecair ionik telah disintesis berdasarkan Magnetic Resonance Nuklear (^{1}H-NMR), Analisis Elemental CHNSO dan Imbasan Elektron Mikroskop (SEM). Data NMR spektroskopi untuk sampel IL adalah: 1H-NMR (500 MHz, DMSO) (ppm): δ 1,08-1,11 (triplet, 0.28H), 1,20-1,23 (triplet, 9.04H), 2.06 (singlet, 0.11H), 2.10 (singlet, 0.03H), 3,09-3,14 (musik untuk enam orang, 6.15H), 3,38-3,4 (Doublet, 0.1H), 8.95 (singlet, 1H), 11.00 (singlet, 3.19H). Pengesteran FFA daripada WCO telah dijalankan dengan menggunakan Et_3NHSO_4 sebagai pemangkin di peringkat pertama pada keadaan tindak balas optimum 60 ° C suhu tindakbalas, 5% berat pemangkin punggah 6:1 nisbah molar metanol kepada WCO selama tiga jam masa tindak balas. Novel pepejal cecair berasid ionik, Et_3NHSO_4 disokong dengan prestasi paparan DVB yang baik dengan menunjukkan 75,94% penukaran FFA. Ia dijangka bahawa pemangkin dikitar semula akan memaparkan sifat yang sama dengan pemangkin segar kerana sifat-sifat yang boleh memudahkan proses pemisahan dari campuran tindakbalas itu. Walau bagaimanapun, hasil FTIR menunjukkan perbezaan data spektrum IR diperolehi untuk pemangkin segar dan pemangkin yag telah digunakan yang menunjukkan bahawa pemangkin tidak terpisah sepenuhnya daripada campuran esterifikasi.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Subscripts

C	concentration
f_0	weight fraction of FFAs in the beginning of the reaction
M	sample weight
M_W	molecular weight
V	volume
X	conversion
AV_0	the initial acid value
AV	acid value

LIST OF ABBREVIATIONS

^{1}H NMR	Proton nuclear magnetic resonance
DVB	Divinyl benzene
FAME	Fatty acid methyl ester
FFA	Free fatty acid
FT-IR	Fourier transforms infrared
IL	Ionic liquid
NMR	Nuclear magnetic resonance
SEM	Scanning electron microscopy
WCO	Waste cooking oil

1 INTRODUCTION

1.1 Motivation and statement of problem

The use of biodiesel can be one of the alternatives in replacing the petroleum-based diesel that is in demand due to the increase in industrialization development and population. Biodiesel or fatty acid methyl ester (FAME) can be classified as nontoxic and biodegradable substitute fuel that can be obtained from renewable sources (Kulkarni and Dalai, 2006). It is mainly produced with transesterification process by using either vegetable oils or animal fats by means of the presence of an acid or base as catalyst that the glycerides react with lower types of alcohol (methanol or ethanol) which then produced a mixture of glycerol, alkyl esters and fatty acids (Araujo et al., 2012). The use of biodiesel has advantages from environmental concerns as it can reduce emission of pollutant gaseous. In producing an economical biodiesel, the major distress is basically the choices of feedstock that has high availability and cheaper.

There are various types of feedstock or raw materials from vegetable and animal sources that can be used in the production of biodiesel. It can be classified into edible and non-edible type of feedstock. The problem that may encountered when choosing the edible type of feedstock such as soybean oil, peanut oil and palm oil was that the production cost might be costly, due to the high cost of raw vegetable oil especially. Therefore, the non-edible feedstock that can be seen in Table 1 is more preferable as it is cheaper.

Table 1-1: Free Fatty Acids (FFAs) content in Various Feedstocks (Jena et al., 2010; Worapun et. al, 2012; Berchmans and Hirata, 2008; Zhang and Jiang, 2008; Zheng et. al, 2006; Russbueldt et. al, 2009; Salimon et. al, 2010; Cowan et. al, 2012; Canoira et. al, 2008).

Feedstocks	Free fatty acid content (%)
Crude mahua oil	13-20
Crude jatropha oil	12-15
Crude jatropha curcas seed oil	15
Crude tobacco seed oil	17
Crude zanthoxylum bungeanum seed oil	25
Waste cooking oil	6-15
Crude palm oil	4.8-7.2
Yellow grease	<15
Brown grease	>15
Animal fat	15
Palm kernel oil	3-7.5

In this present years, it can be seen that there are huge amount of waste cooking oil (WCO) that were not properly managed which mainly came from restaurants, food processing company and food industries that had regrettably contributed to the environmental concerns. Therefore, using WCO as a feedstock is a wise choice based on the economic factor and environment issues. However, the problem when using WCO as the feedstock was that it basically has high free fatty acids (FFAs), due to hydrolysis of triglycerides through frying (Gan et al., 2012). Previous study has clarified that in alkaline transesterification reactions (biodiesel production process), the oil or fat used must contain not more than 1-2% FFAs, which is similar to about 2 mg KOH/g triglyceride. In this matter, saponification has lowered the yield and formation rate of FAME if the FFA level exceeds the 2% FFAs content that may cause difficulties in separation process and catalyst reutilization. (Berrios et al., 2007; Abidin et al., 2012). Thus, WCO need to go through the acid catalysed esterification in lowering the FFAs content.

The type of acid that frequently used in the esterification process was basically the sulphuric acid or hydrochloric acid (homogenous acid catalyst) as it has high conversion properties and also low cost. The major concern when using this type of acid or homogenous catalyst is due to the effluent disposal inconvenience and catalyst-loss reason. Plus, the chemical properties of acid that can cause corrosion also have lead to the high equipment cost. Thus, this problem has brought into the research of using heterogenous-based catalyst in the esterification reaction (Gan et al., 2012). Examples

of heterogenous type of catalysts are ion-exchange resins, activated carbon, zeolites and acidic ionic liquids (ILs).

ILs have garnered much attention during these years due to its outstanding properties. The advantages of ILs are that it has high conductivity, broad electrochemical window, sturdy dissolution activity and insignificant volatile pressure (Liang et al., 2012). Moreover, acidic ILs including the Lewis and Bronsted ones also has high activities in acid-catalytic reactions. Although the efficiency of the esterification process can be obtained due to the uses of ILs, but it have some disadvantages as it can cause purification difficulty due to its certain solubility. Therefore, the solid supported types of ionic liquids or novel solid acidic ionic liquids are more preferable in the esterification process.

Based on the previous research, Qiao et al. (2006) had explained that the ionic liquids are basically supported by immobilizing the chloroaluminate based ionic liquid on solid support through the process of chemical covalent bond (substantial coating on Al_2O_3, SiO_2, and TiO_2 or covalent attachment of ionic liquids on the surface of the support such as polystyrene, silica gel, zeolite, and divinylbenzene). The advantages of supported ionic liquid compared to the unsupported one are it plus side on the separation, reusability as well as its capability in providing practical amenities in a continuous system (Xu et al., 2010).

Therefore, this research will concentrate on the esterification of free fatty acids from waste cooking oil using novel solid acidic ionic liquid as catalyst.

1.2 Objectives

The following are the objectives of this research:

1. To synthesize and characterize the solid acidic ionic liquids (ILs) supported with divinylbenzene (DVB).
2. To study about the esterification of free fatty acids (FFAs) from waste cooking oil (WCO) using novel solid acidic ionic liquid as catalyst.

1.3 Scope of this research

In this research, it focused more on synthesizing the catalyst, Bronsted acid ionic liquid (Et_3NHSO_4) supported with DVB. Catalyst characterization is done by Nuclear

Magnetic Resonance (^{1}H-NMR), Fourier Transform-Infra Red (FT-IR), elemental analysis and Scanning Electron Microscopy (SEM) methods in finding the confirming the immobilization of the active component on the support, characterize the supported ionic liquid polymer and to determine unknown sample based on molecular weight and the effect of cleaning regimes on the surface of the DVB supported Et_3NHSO_4 ionic liquid catalysts for the single formulation of supported ionic liquid polymer.

The esterification of FFAs from simulated waste cooking oil (WCO) using novel acidic polymer as catalyst was studied at optimum reaction condition of 60°C reaction temperature, 5 wt % catalysts loading and 6:1 methanol to WCO molar ratio for three hours of reaction time.

2 LITERATURE REVIEW

2.1 General Overview

These days the diesel fuel is in high demand in various industries and also in automobiles. Nevertheless, the price for the petroleum-based diesel kept growing and people are concerned about the negative effect of this type of fuel towards the environment (Worapun et al., 2012). There are a lot of research that has been made in order to find the suitable renewable sources to replace petroleum-based diesel and the researchers has agreed that biodiesel one of the most advantages type of diesel to be choose from (Nogueira et al., 2010). The discovery of biodiesel begin in the 1890s in Germany by Rudolph Diesel, when he was in search for the fuel to power early diesel engines for agriculture where at that present time the petroleum still has not yet been discovered. A lot of improvement has been made since then in order to produce the most beneficial type of diesel. In producing an economic type of biodiesel, the major concern is basically the type of feedstock to choose from and the suitable methods and materials (type of catalyst especially) for the process as depending on the different processes, they may present with variations of technical challenges.

2.2 Introduction

This paper presents the experimental studies of esterification of free fatty acid in waste cooking oil using novel solid acidic ionic liquid. This study is conducted in order to produce a more economic and efficient biodiesel as an alternative to replace fossil-based fuels. More thorough explanations will be clarified regarding the significance of this study in this chapter.

2.3 Biodiesel

The production of biodiesel that has rise from just 500 gallons in 1999 to 450 million gallons till the year of 2007 in the United States shows that it plays a big part in order to diversify the existing fuel that are slowly depleting and it is assumed that the production will gradually increase within the years (Chand et al., 2009). Biodiesel or Fatty Acid

Methyl Esters (FAME) is basically consisting of alkyl esters of fatty acids. Generally, biodiesel is yield from the transesterification process which is the reaction of triglycerides and alcohol such as methanol with the presence of base or acid catalyst (Wahlen et al, 2012).

This type of diesel that basically derived from renewable biological sources (vegetable oils and animal fats) has many advantages compared to the fuel in the present markets. From the previous studies, it has been found that biodiesel is environmentally friendly as it was able to lessen the pollutant gaseous (Gan et al., 2012). In comparison with the conventional fuels, biodiesel provides cleaner engine emission and this can be proved by the recent researched which states that there are reduction of unburned hydrocarbon particulate and carbon monoxide emissions (Yin et al., 2012; Wahlen et al., 2012). Plus, biodiesel is also biodegradable as it has shorter half-life in comparison with petroleum diesel. Because of its high solubility and biodegradation, biodiesel may also be one of the alternatives to be used in bioremediation in removing oils or polycyclic aromatic hydrocarbons (PAHs) in contaminated soils (Chien et al., 2009). Other than that, biodiesel is advantageous in engine lubricity as it provides better performance rather than the common diesel. The lubricity of diesel fuel was important in providing the protection for better performance. This is vital, as there have been plentiful examples from the field where lack of lubricity in the fuel has caused premature equipment breakdowns and in some cases, catastrophic failures ("Lubricity Benefits", 2013). Moreover, the availability of the feedstock also gives a huge benefit in the production of biodiesel. There are varieties of feedstock (vegetable oils, animal fats, and waste cooking oils) in synthesizing the biodiesel. Typically, the main feedstock for biodiesel production is refined vegetable oils. However, the prices of these refined vegetable oils have been gradually increased over the past few years, which have caused the biodiesel production from this feedstock is unbeneficial.

2.4 Renewable Energy Sources: Feedstock

The availability and sustainability of sufficient supplies of less costly feedstock will be a fundamental factor in commercializing biodiesel to compete with other type of diesel. As has been mention before, there are several types of feedstock that can be used in producing biodiesel and it can be categorized into two parts which are edible feedstock and non-edible feedstock that includes of vegetable oil and animal fat.

2.4.1 Vegetable Oil

Biodiesel produced from vegetable oils can be used as an alternative diesel fuels because of its characteristics that are approximately similar to the petroleum-based fuels. For instance, they have the same viscosity value as the petroleum-based diesel fuel, their volumetric heating values are a bit lower, however their cetane number and flash points are quite high. The basic constituent of vegetable oils is triglyceride. As can be seen in Scheme 1, it shows the example of typical triglyceride molecule. Vegetable oils basically consist of 90 - 98% triglycerides and small amounts of mono- and diglycerides.

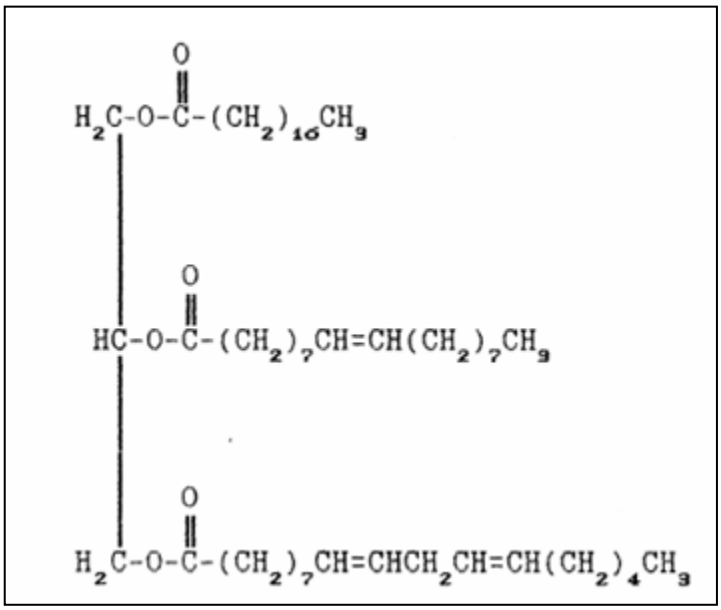


Figure 2-1: Structure of typical triglyceride molecules

These vegetable oils such as palm oil, soybean oil, peanut oil, sunflower seed oil, and cottonseed oil are widely used for the production of biodiesel, but most of this edible type of feedstock requires higher processing cost and the feedstock price itself are costly for most countries. As a future prospective fuel, the right choice of its raw materials must be always based on technical and economical aspects.

2.4.2 Animal Fats and Grease

Waste greases and animal fats can also be used as feedstock because of their availability and low cost. The use of animal fats without modification can improve fuel oil's

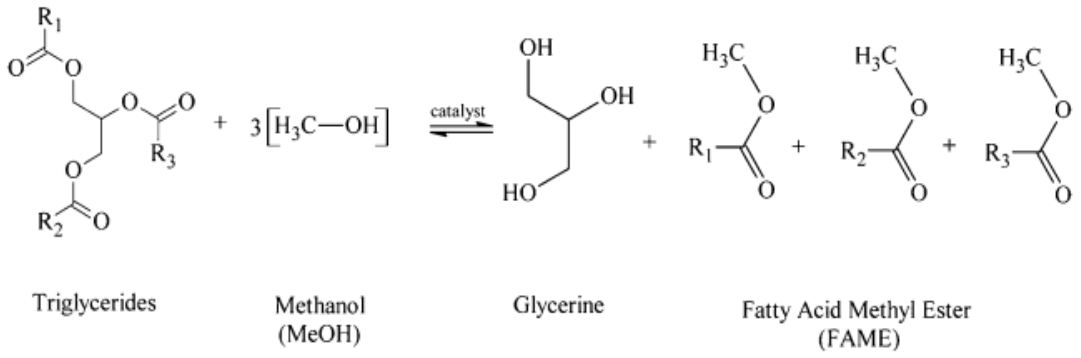
rheological properties. The problems that has arise where these waste greases ended up being disposed and can only be used in the soap industry can be solved by making it as the raw material in biodiesel production. Besides, animal fats are classified as low quality feedstock contrast to the refined vegetable oils due to their free fatty acids (FFA) content that may increase up to 15 wt % by contrast with refined soybean oil, which typically contains less than 0.5 wt % FFA (Canoira et al., 2008). The price of this yellow animal fat is around 419 euros/ton in contrast to the 2007 price of soybean oil of 780 euros/ton ("Agra Informa Ltd") and probably increasing throughout the year. The use of waste animal fat feedstock for biodiesel production is a smart way in lowering the overall biodiesel production costs due to this price difference. Plus by using this type of feedstock has the advantages in various aspects such as quality, engine performance, and environmental problems.

2.4.3 Waste Cooking Oil (WCO)

The use of sustainable feedstock such as waste cooking oil (WCO) has become a main research distress due to the need to replace the used of edible vegetable oils as the biodiesel raw material despite the fact that the production of these vegetable oils has increase over the years. It has found out that the increase in industrial waste oil has caused the disposal problems to arise (Zhang et al., 2003) which has led to the environmental concern. Thus, this problem may be overcome by using these disposals as the feedstock for the biodiesel production. These low cost raw materials such as non-edible oil and WCO that representing 70% of the present biodiesel production cost (Demirbas, 2009) is likely popular among the researchers as a benefiting source to be used as the feedstock. The price of these WCO can be 2.5 to 3.5 times lower than the refined vegetable oil. Several studies have been carried out on biodiesel production from various oils that concentrate on type of oil, temperature of reaction, types of; ratio of alcohol to WCO, free fatty acid and moisture content. All of these factors are the critical aspect in the biodiesel production.

2.5 Production of Biodiesel

In the production of biodiesel, transesterification is one of the most commonly used methods. The reaction for the biodiesel process can be seen in Scheme 1 below.



[a]R_1, R_2, and R_3 represent the fatty acids groups attached to the backbone of triglycerides.

Figure 2-2: General Reaction Scheme for Biodiesel Production[a] (Abidin et al., 2012)

2.5.1 Transesterification

Transesterification process is a process where catalyzed chemical reaction involving vegetable oil and an alcohol to yield fatty acid alkyl eters and glycerol. Triacylglycerols, as the main component of vegetable oil, consist of three long chain fatty acids esterified to a glycerol backbone. When triacylglycerols react with an alcohol, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters, the three fatty acid chains are released from the glycerol skeleton and combine with the alcohol to yield fatty acid alkyl esters. Glycerol is the by-product of the process. Methanol is the most commonly used alcohol because of its low cost and is the alcohol of choice in the processes. Generally in a typical biodiesel reaction process, low temperatures will result in lower conversion, while higher temperatures lead to excessive methanol loss due to evaporation (boiling point of methanol is 64.7 °C). In base-catalyzed transesterification reaction, feedstock (oils and fats) of high FFAs content cannot be directly used. From the previous study, the FFAs content cannot be at least greater than 2% as the conversion of ester may be decrease if it is higher than that (Berrios et al., 2007). This is due to the stable emulsions are formed during saponification process which has lead to problems in separation process and also catalyst reutilization.

2.5.2 Esterification

Esterification is a chemical reaction where two reactants, an alcohol and an acid form an ester as the final product of reaction. It is a reversible reaction, thus many esterification reactions can be considered as equilibrium reactions. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel, and crude glycerol. Usually, methanol or ethanol is the alcohol used in the production where methanol produces methyl esters and ethanol produces ethyl esters where as potassium or sodium hydroxide is the base catalysed. Scheme 2.3 shows the reaction for esterification process where FFA is converted to FAME.

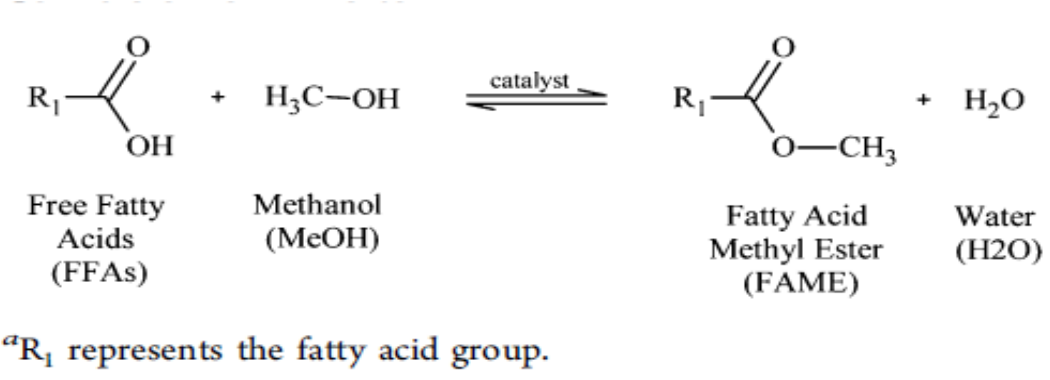


Figure 2-3: Reaction Scheme for Esterification Process: Conversion of FFA to FAME (Abidin et al., 2012)

2.6 Processes Variables Effecting Esterification

2.6.1 Catalyst

In obtaining vegetable oils with high quality, the alkaline catalysts show high performance, but the major concern is that the oils have quite number of FFA which cannot be converted into biodiesel but produce soap instead (Cardoso et al., 2008). Other option to process these vegetable oils is by using a Brønsted and Lewis acid catalyst. Nevertheless their high cost and high viscosities limited their applications in the industries.

2.6.1.1 Homogenous Catalyst

In the present years, homogenous acid types of catalyst are widely used in the biodiesel processes. The most common catalyst are sulphuric (H_2SO_4) acid and hydrochloric (HCl) acid. These types of catalyst have it disadvantages as it is soluble in the methanol. Some of the drawbacks that has arise by using this type of catalyst are it can cause the equipment to be corrosive, side reactions may exists, a substantial amount of wastewater may be generated, a high cost production due to supplementary equipment or reagents for separation or neutralization processes, and problems in catalyst reusability (Abidin et al., 2012).

2.6.1.2 Heterogenous Catalyst

Heterogenous type of catalyst such as zeolites, activated carbon, ion-exchange resins, single and mixed metal oxides and organic acid catalysts is the most suitable in the biodiesel processes (production and purification) due to its superficial properties that can ease the separation process from the reaction mixture. Therefore, the catalyst will able to be recycled for several times. Plus, this will lead to the waste reduction from the biodiesel production and lessen the environmental problems. Nevertheless, despite all of these advantages, the heterogenous type of catalyst also has it drawbacks in the terms of causing purification difficulty due to its certain solubility. In order to solve this problems further researched has been made on the investigation of supporting acid catalyst (ionic liquids) supported onto the surface of solid support (DVB). The supported acid catalysts has many advantages in comparison with the unsupported one as the separation process will be less difficulties, it has higher reusability and it will be very practically for the continuous process (Xu et al., 2010).

a) Zeolites Catalyst

Zeolites are popular catalysts for organic synthesis. General advantages for zeolites are that they can be synthesized with different crystal structures, framework Si/Al ratios, and proton exchange levels. This level of control when synthesizing zeolites makes it possible to maintain different properties such as size and structure of pores, strength of acid sites and their distribution, and surface hydrophobicity which offers

the additional advantages in achieving effective segregation of water which otherwise is reported to poison the catalyst acid sites. Although zeolites are active catalysts for esterification, they catalyze the reaction rather slowly due to the steric hindrance associated with bulky fatty acids, or due to poor adsorption inside zeolite pores. Plus, even though zeolite catalysts show high activity, the reaction always gives a variety of undesired by-products due to the use of higher reaction temperatures. Scheme 4 shows the basic structure of zeolite.

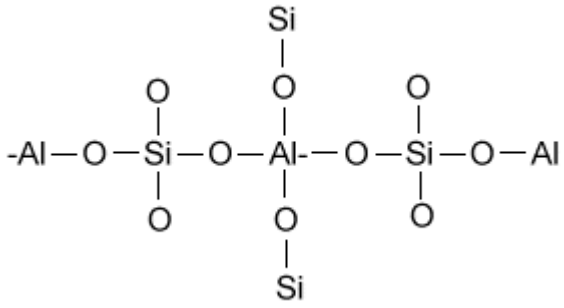


Figure 2-4: Basic structure of zeolite

b) Activated Carbon Catalyst

Multiplicity of reactions can be catalysed by using carbon. Due its low cost and variations of distinct physicochemical properties and morphologies, carbons are anticipated catalytic materials. Plus, as a catalyst support in liquid and vapour phase reactions, activated carbon is proven to be extremely effective (Buasri et al., 2012). The advantages of this catalyst are that it has a large surface area that lets the catalyst to diffuse over efficiently besides can be produced from a variety of raw materials.

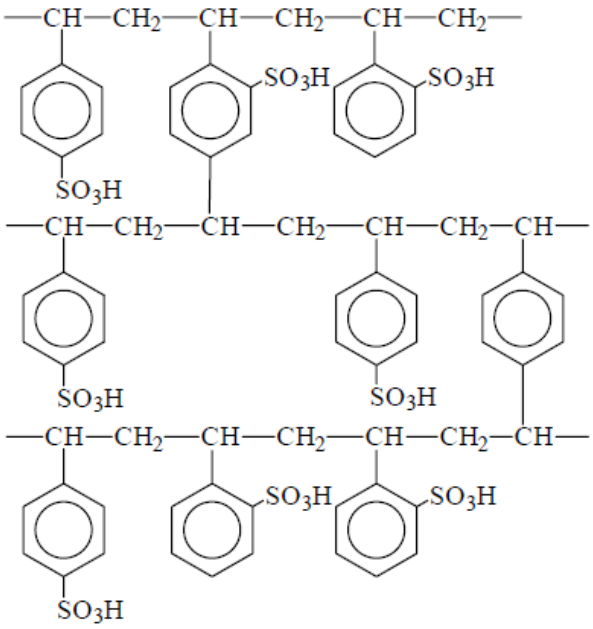
Figure 5.2 shows the close up figure of activated carbon.

Figure 2-5: Close up figure of activated carbon

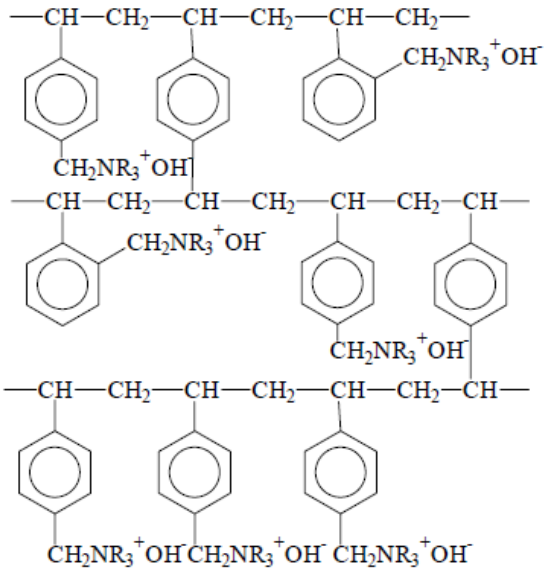
c) Ion-exchange Resins Catalyst

Ion-exchange resins are a type of polymers. They act by exchanging particular ions within the polymer with ions in a solution that is passed through them. The synthetic resins are used primarily for purifying water, but also for various other applications including separating out some elements.

Ion exchange materials are insoluble substances containing loosely held ions which are able to be exchanged with other ions in solutions which come in contact with them. These exchanges take place without any physical adjustment to the ion exchange material. Ion exchangers are insoluble acids or bases which have salts which are also insoluble, and this enables them to exchange either positively charged ions (cation exchangers) or negatively charged ones (anion exchangers). Scheme 2.5 below shows some structures of ion-exchange resins.



A strongly acidic sulphonated polystyrene cation Exchange resin



A strongly basic quaternary ammonion anion exchange resin

Figure 2-6: Some examples of ion-exchange resins

Ion-exchange resins such as Amberlyst-15 and Nafion® are assured to be active catalysts for esterification due to its properties that have medium acid strength. Nevertheless, they have some drawbacks which the sulfonic acid cation exchange resins are not stable at temperatures higher than 140°C that inhibits the implication of these catalysts in a reaction that run at higher reaction temperature and they show

less activity due to diffusion limitations although they contain highly acidic sites in the reaction of carboxylic acids with long chains of hydrocarbon moieties (Suwannakarn, 2008).

d) Silica Mesoporous Catalyst

Silica mesoporous materials modified with sulfonic groups are utilized in pretreatment esterification reactions of high free fatty acid oils. This type of organic hybrid mesoporous silicas functionalized with sulfonic acid groups have shown successful results for acid catalyzed esterification by incorporating functionalized organic groups (Hermida et al., 2008). The hydrophobic character of SO_3H-mesoporous materials is beneficial for the overall conversion and selectivity. Fine tuning of catalyst hydropobicity has been achieved by introducing methyl groups on the catalyst surface by a variety of well-known procedures. Figure 2.2 shows the structures of mesoporous M41S family of silica and aluminosilicates.

Figure 2-7:Structures of Mesoporous M41S Family: a. MCM-41 (2D hexagonal, space group p6mm); b. MCM-48 (cubic, space group $Ia\bar{3}d$); c. MCM-50 (lamellar, space group p2) (Hoffman et al., 2006)

e) Solid Supported Ionic Liquid Catalyst

Ionic liquid (IL) is a constituent that composed utterly of ions which appear in a liquid phase at room temperature. The IL comprises of organic cations and inorganic anions, even though it is not restricted to these combinations. IL is believed to have melting point of less than 100 ºC, or accurately less than 50ºC, beside the fact that the IL can have a high melting temperature such as in the case of the molten salt form of NaCl. Due to the outstanding properties of ILs such as high conductivity, slight volatile pressure, wide electrochemical window and strong dissolution ability it has received high interest over the years. ILs of huge quantity have been applied in

the chemical synthesis where the ILs are used as solvents or as the catalysts (Liang et al., 2012).

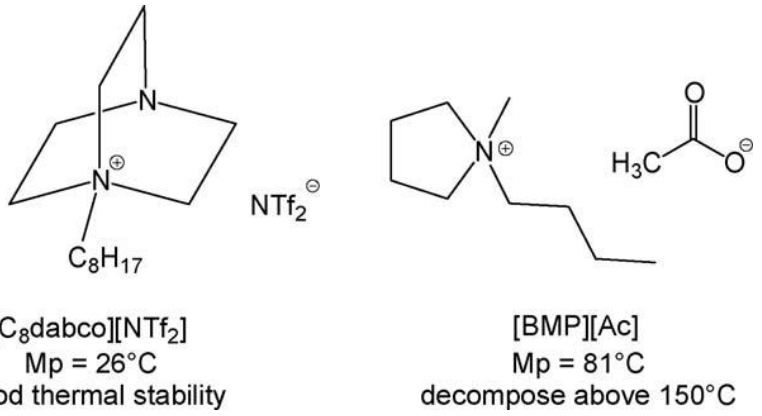


Figure 2-8: Examples of Basic ILs structure

The sulfonic acid groups functionalized ionic liquids owned high activities for acid-catalytic reactions (Sugimura et al., 2007). There are still some drawbacks even though the efficient procedures for various reactions (esterification, acetalization, and alkylation) are developed using the ILs. For an example, as certain solubility with some organic compounds, especially the polar molecules, this not only made the catalyst loss, but also had caused difficulty in the purification. Hence, the immobilization of ILs is a wise option. Some of the solid supported ionic liquid examples are where the acidic ionic liquids were immobilized on silica–gel and it high activities for acetalization were obatained (Miao et al., 2011). The sulfonic acid functionalized acidic ionic liquid modified silica catalyst was prepared and shown to be effective in the hydrolysis of cellulose The polystyrene supported acidic ionic liquid showed high activities for esterifications (Xu et al., 2010). Besides the expensive reagents were used for the synthetic procedure, the recycled catalytic activities of the immobilized ionic liquid dropped a lot. The acidic molecules were dispersed on the surface, which decreased the synergistic effect. On the other hand, the acidic sites attached to the surface easily fell off, which made the recycled activities drop quickly. Polymeric ionic liquids which is a new class of materials, has develop an outstanding properties as electrolytes for electrochemical devices (Yamada et al., 2009). For this research, novel acidic polymeric ionic liquid from Brønsted acidic ionic liquid triethylammonium hydrogen sulphate (Et_3NHSO_4) and divinylbenzene (DVB) was studied. In order to confirm the cooperative effect of the ions, the monomer was polymerized and afterwards the oligomers were copolymerized with DVB. For the high polarity Ionic liquid was difficult to form the solid polymer. The use of DVB as the high hydrophobic BET